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A. S. Cheng, B. A. Buchholz, R. W. Dibble

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Isotopic Tracing of Fuel Carbon in the Emissions of a Compression-Ignition Engine Fueled With Biodiesel Blends

A. S. (Ed) Cheng

California State University, Sacramento

Bruce A. Buchholz

Lawrence Livermore National Laboratory

Robert W. Dibble

University of California, Berkeley

ABSTRACT

Experimental tests were conducted on a Cummins B5.9 direct-injected diesel engine fueled with biodiesel blends. 20% and 50% blend levels were tested, as was 100% (neat) biodiesel. Emissions of particulate matter (PM), nitrogen oxides (NO_x), hydrocarbons (HC) and CO were measured under steady-state operating conditions. The effect of biodiesel on PM emissions was mixed; however, the contribution of the volatile organic fraction to total PM was greater for the higher biodiesel blend levels. When only non-volatile PM mass was considered, reductions were observed for the biodiesel blends as well as for neat biodiesel. The biodiesel test fuels increased NO_x , while HC and CO emissions were reduced.

PM collected on quartz filters during the experimental runs were analyzed for carbon-14 content using accelerator mass spectrometry (AMS). These measurements revealed that carbon from the biodiesel portion of the blended fuel was marginally less likely to contribute to PM, compared to the carbon from the diesel portion of the fuel. The results are different than those obtained in previous tests with the oxygenate ethanol, which was observed to be far less likely contribute to PM than the diesel component of the blended fuel. The data suggests that chemical structure of the oxygen-carbon bonds in an oxygenate affects the PM formation process.

INTRODUCTION

The use of reformulated, cleaner-burning fuels is among the strategies being pursued to reduce emissions from compression-ignition (diesel) engines. Among the fuels being investigated, blends of oxygenated compounds and conventional diesel fuel show particular promise due

to their ability to substantially reduce PM emissions. Additional benefits can be realized with oxygenated diesel fuels when the oxygenated compound is derived from domestic and/or renewable sources.

Although the PM emissions benefits of oxygenated diesel are well known, much remains unknown about the mechanisms through which oxygenates reduce PM. For example, there is disagreement among researchers about whether fuel oxygen content is the dominating factor that controls the level of PM reduction.

Accelerator mass spectrometry (AMS) has recently been utilized to provide insight into PM formation during oxygenated diesel combustion [1,2]. AMS is a measurement technique developed in the late 1970's as a tool for tracing long-lived radioisotopes in chronometry in the earth sciences and archeology fields (e.g., carbon-14 (^{14}C) dating of fossil remains). The technique is extremely effective in detecting small ^{14}C levels.

AMS allows for fuel-specific isotope tracing by exploiting the natural difference in ^{14}C content between a fuel produced from contemporary (i.e., recently living) materials and petroleum-derived diesel fuel. For an engine operated on a blend of these fuels, the ^{14}C content of exhaust emissions can be measured to identify the relative contribution to emissions from each fuel component.

In the current study, the contribution of fuel components to non-volatile organic PM mass is investigated using isotopic tracing. Biodiesel, manufactured by the esterification of vegetable oil, was used as the contemporary fuel component. Blends of 20% and 50% biodiesel (by volume) in a baseline diesel fuel were tested using a Cummins B5.9 engine. 100% (neat) biodiesel was also tested, and conventional emissions

measurements were made to evaluate the impact of biodiesel on regulated emissions.

MATERIALS AND METHODS

EXPERIMENTAL APPARATUS

The test engine is a Cummins B5.9 4-stroke, direct-injected, turbocharged and aftercooled engine rated at 130 kW (175 hp). Engine specifications are listed in Table 1. The engine utilizes a mechanical fuel injection system (Bosch P7100 PE type) that provides injection pressures of up to 115 MPa. No modifications were made to the engine or fuel injection system to optimize for operation on the test fuels.

Gaseous emissions were monitored with Horiba gas analyzers employing chemiluminescence (NO_x), flame ionization (HC), and infrared absorption (CO). PM mass measurements were made using a partial flow, mini-dilution tunnel designed and constructed at the University of California, Berkeley. 47 mm Pallflex 2500QAT-UP quartz filters were used for PM collection and were pre-combusted at 900 °C for 3 hours to remove all residual carbon.

^{14}C measurements were conducted at the Center for Accelerator Mass Spectrometry at Lawrence Livermore National Laboratory, using an HVEE FN system operating at 6.5 MV. The system uses a cesium-sputter ion source to produce negative ions from a graphite sample prepared from the PM carbon. A low energy mass spectrometer selects for mass 14 ions (^{14}C , $^{13}\text{CH}^+$, $^{12}\text{CH}_2^-$), and the molecular isobars of ^{14}C are then removed in the electron stripper at the accelerator terminal. A multiple anode gas ionization detector identifies the nuclear isobars and counts individual ^{14}C atoms. Further details regarding the AMS measurement procedure can be found in Reference 3.

TEST FUELS

The baseline diesel fuel (D2) used in the tests was a CARB-certified no. 2 diesel fuel with a sulfur content of 125 ppm. Additional baseline diesel fuel properties are shown in Table 2. The biodiesel was vegetable oil-derived and met published ASTM fuel specifications [4]; the specifications include a minimum cetane number of 47. A representative composition of the biodiesel fuel, as provided by the manufacturer (Cytoculture International, Inc.) is given in Table 3.

In addition to the baseline diesel and neat biodiesel (B100), blends of 20% biodiesel (B20) and 50% biodiesel (B50), by volume, were prepared for testing.

The ^{14}C content of all four test fuels were measured before engine testing began; results are listed in Table 4. As expected, the ^{14}C content of the biodiesel was much larger (by a factor of over 1300) than that of the

baseline diesel fuel. The oxygen content of each test fuel is also indicated in Table 4.

TEST PROCEDURES

Engine testing was conducted at a single steady-state operating condition of 285 N-m (210 ft-lbs) at 1600 rpm. During fuel changes, the engine was operated on the new test fuel for a minimum of 30 minutes prior to data collection.

Gaseous emissions were recorded via a PC-based data acquisition system. For the PM measurements, blank filters were conditioned to temperature and humidity overnight in petri dishes and individually weighed on a Mettler UM 3 microbalance. Filter sampling was carried out at a dilution ratio of 6.5, as determined by measurement of CO_2 concentrations in both the raw and diluted exhaust. Four separate samples were collected for each test fuel.

In addition to the total PM mass measurement, loaded filters were subsequently processed to separate the volatile organic fraction (VOF) from the non-volatile organic fraction (NVOF). One half of each filter was directly converted to an AMS sample via graphitization with a CuO oxidizer (complete details on the AMS sample preparation methodology can be found in Reference 5). The other half was heated in a furnace at 340 °C for 2 hours to remove the VOF. The remaining NVOF is then converted to an AMS sample via the same graphitization procedure. During sample preparation, CO_2 pressures from the completely combusted samples were measured and represent the carbon mass of each sample. The VOF is then estimated by the difference in carbon mass between the non-treated half-filter and the heated half-filter.

RESULTS AND DISCUSSION

ENGINE-OUT EMISSIONS

PM and NO_x emissions results for each test fuel are presented in Figures 1 and 2. Error bars in the figures represent a 95% confidence interval in the measured value. Tables 5 and 6 provide a complete summary of all engine-out emissions for the test fuels. Results are reported both in terms of absolute values (g/kW-hr) as well as normalized to the baseline diesel fuel. Note that the g/kW-hr values for NVOF and VOF in Table 4 were obtained by simply multiplying the experimental values for NVOF and VOF (in terms of a fraction or percent) by the g/kW-hr value for total PM.

In terms of total PM mass, the effect of biodiesel addition was mixed. For the B20 fuel, a PM reduction of 27% was observed. For B50, no statistically significant change was recorded, and for B100, PM mass actually increased. Upon inspection of the NVOF results, however, it is apparent that much of the PM mass at the higher

biodiesel blend levels is due to the contribution of volatile compounds. For example, for the baseline diesel fuel, 58% of total PM mass was attributed to the NVOF; for B100, only 18% of total PM mass was contributed by the NVOF. The large VOF for B100 can probably be attributed to unburned hydrocarbons derived from the biodiesel fuel and water condensation and adsorption, under the particular dilution conditions of these tests. Since a significant reduction in inorganic PM mass does occur, greater benefits (from the standpoint of total PM) could be achieved through the use of biodiesel in combination with a PM oxidation catalyst.

The NO_x emissions results shown in Figure 2 and Table 5 indicate that biodiesel addition increases NO_x formation. B20 and B50 increased NO_x emissions by 3% and 6%, respectively, while B100 produced a 13% increase in NO_x. These NO_x increases are consistent with results reported by other researchers [6-10]. Senatore et al. report that the use of biodiesel advances the heat release rate in diesel engines [10]. Therefore, an increase in thermal NO_x production due to higher in-cylinder combustion temperatures are the probable cause of the higher engine-out NO_x emissions.

Although HC and CO emissions are typically low from diesel engines, test results show that significant reductions in both of these emissions are achieved with biodiesel. This may be of importance in terms of air quality issues in certain regions or with regards to the combined NO_x + HC emissions standard.

¹⁴C ISOTOPE ANALYSIS OF NVOF PM

The ¹⁴C isotope analysis conducted using AMS techniques was carried out only on the NVOF of the collected PM samples. This was because the current investigation focuses on the nature of PM formation during the in-cylinder combustion process. The VOF, formed primarily in the exhaust and dilution processes, was not considered. Throughout the remainder of this subsection, the term PM will implicitly refer only to NVOF PM. In addition, since the ¹⁴C measurements reveal the relative contribution to emissions from each component of a blended fuel, analysis was only carried out on PM samples from the B20 and B50 fuels (by definition, all PM that can be attributed to the fuel comes from diesel for the baseline diesel fuel, and from biodiesel for the B100 fuel).

The isotope ratios (*R*) of ¹⁴C to total C for each analyzed PM sample can be expressed as

$$R_{sample} = \frac{{}^{14}C_{sample}}{{}^{12}C_{sample}} = \frac{{}^{14}C_D + {}^{14}C_B + {}^{14}C_{oil}}{{}^{12}C_D + {}^{12}C_B + {}^{12}C_{oil}} \quad (1)$$

where the subscripts *D* and *B* indicate the contributions from diesel and biodiesel, respectively. Note that the contribution from lubrication oil is also considered. Since

both the baseline diesel fuel and the lubrication oil are petroleum-derived, their contribution to the ¹⁴C content of the sample can be neglected. In addition, a separate analysis conducted by the authors indicate that approximately 4% of the total carbon mass in the PM is contributed by the lubrication oil [11]. Thus, Eq. (1) can be rewritten

$$R_{sample} = \frac{{}^{14}C_B}{1.04(C_D + C_B)} \quad (2)$$

The ¹⁴C in the PM sample is assumed to be contributed only by the biodiesel, and can be expressed as the isotope ratio of the biodiesel fuel (*R_B*) multiplied by the total biodiesel carbon in the sample, i.e.,

$${}^{14}C_B = R_B C_B \quad (3)$$

Eqs. (2) and (3) can then be solved for the fraction of the PM mass attributable to the biodiesel (*F_B*). The result is

$$F_B = \frac{C_B}{C_B + C_D} = 1.04 \frac{R_{sample}}{R_B} \quad (4)$$

Note that this value considers the total carbon mass to be the PM carbon that originates from the fuel components. The contribution of lubrication oil to PM appears in the factor of 1.04 with the isotope ratios.

The calculation represented by Eq. 4 was carried out for each of the PM samples collected for the B20 and B50 test fuels. Results were averaged for each test fuel and are presented in Figure 3 and Table 7. Table 7 also includes the relative probability, *P*, that carbon derived from the biodiesel produces PM, compared to the baseline diesel. This is defined as the fraction of biodiesel in the PM divided by the fraction of biodiesel in the fuel. The relative probability can also be expressed as

$$P = \frac{\begin{array}{c} \text{carbon mass fraction} \\ \text{from biodiesel in PM} \end{array}}{\begin{array}{c} \text{carbon mass fraction} \\ \text{from biodiesel in test fuel} \end{array}}$$

If every carbon atom in a test fuel was equally likely to participate in PM formation, then the results should reveal that *P* ≅ 1. If the carbon from the biodiesel played no role in soot formation, then a value of *P* ≅ 0 should be observed.

The relative probabilities calculated for B20 and B50 were 0.94 and 0.92, respectively. These results indicate that carbon from the biodiesel portion of the fuel contributed to PM formation with slightly less probability than the carbon from the diesel portion of the fuel. In previous tests with ethanol-diesel blends, however, the

authors observed much lower relative probabilities of 0.50 and 0.59 for 10% and 20% ethanol, respectively (Table 8).

Inspection of the composition of the biodiesel fuel (Table 3) and the chemical formula of ethanol (C_2H_5OH) reveal that ~11% of biodiesel carbon is bonded to an oxygen atom while 50% of ethanol carbon is bonded to an oxygen atom. The oxygen in biodiesel appears as a methyl ester at the end of C_{16} - C_{18} hydrocarbons while the oxygen in ethanol occurs as an alcohol. If the oxygen adjacent to a carbon atom always took that carbon to CO_2 , with no other effects on the combustion event, the relative probabilities in Tables 7 and 8 for biodiesel and ethanol would be 0.89 and 0.50, respectively. Because the relative probabilities are higher, the oxygen is less effective in oxidizing the carbon. Increased production of soot precursors or non-optimal distribution of oxygen among carbon in the oxygenate could account for this effect.

CONCLUSION

The results of experimental tests on a Cummins B5.9 engine indicate that biodiesel blends and neat biodiesel have a mixed effect on total PM emissions. However, biodiesel tended to produce PM with higher VOF, and thus significant reductions in NVOF were achieved with biodiesel addition. The results suggest that biodiesel can most effectively reduce PM when used in combination with a PM oxidation catalyst.

NO_x emissions for the biodiesel blends increased between 3% and 6%, and neat biodiesel produced 13% higher NO_x than the baseline diesel fuel. For all of the biodiesel test fuels, HC and CO reductions were observed.

Results of ^{14}C isotope analysis on the NVOF PM using accelerator mass spectrometry revealed that, for the biodiesel blends, the biodiesel fraction of the fuel was slightly less likely to contribute to PM as compared to the diesel portion of the fuel. When viewed along with previous results obtained with ethanol-diesel blends, the results indicate that the distribution of carbon-oxygen bonds in an oxygenate may influence the effectiveness of the oxygenate to reduce PM. The data implies that the chemical structure of an oxygenate impacts its PM reduction potential.

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DEFINITIONS, ACRONYMS, ABBREVIATIONS

^{14}C : carbon-14 isotope

amol: attamole = 1×10^{-18} mole

AMS: accelerator mass spectrometry

B20: 20% biodiesel (by volume) blended with the baseline diesel fuel

B50: 50% biodiesel (by volume) blended with the baseline diesel fuel

B100: 100% (neat) biodiesel

E10: 10% ethanol (by volume) blended with the baseline diesel fuel

E20: 20% ethanol (by volume) blended with the baseline diesel fuel

D2: baseline diesel fuel

HC: hydrocarbons

NO_x: oxides of nitrogen (NO + NO₂)

NVOF: non-volatile organic fraction

PM: particulate matter

VOF: volatile organic fraction

Table 1. Cummins B5.9 engine specifications.

Model year	1993
Configuration	6 cylinder inline
Displacement	5.88 liters (359 in ³)
Horsepower rating	175 hp @ 2500 rpm
Torque rating	420 ft-lb @ 1600 rpm
Aspiration	turbocharged and aftercooled
Bore	102 mm (4.02 in)
Stroke	120 mm (4.72 in)
Compression ratio	17.6:1
Injection timing	11.5° BTDC

Table 4. Experimental test fuels.

Test fuel	Designation	¹⁴ C content (amol ¹⁴ C/mg C)	Oxygen content (% by mass)
Baseline diesel	D2	0.0783	0.0
20% biodiesel	B20	20.2	2.3
50% biodiesel	B50	50.2	5.6
100% (neat) biodiesel	B100	103	11.0

Table 2. Fuel analysis results for baseline diesel fuel.

Test	Result
Density (kg/L @ 20 °C)	0.8425
Viscosity (cSt @ 40 °C)	3.27
Cetane number	49.2
Sulfur (ppm)	125
Aromatics (wt. %)	16.1
Polynucleic aromatics (wt. %)	4.0
Distillation (°C)	
IBP	175
10%	221
50%	277
90%	332
95%	347
EP	360

Table 3. Representative composition of biodiesel fuel.

Compound	% by mass
Methyl linoleate CAS 112-62-9 $\text{CH}_3(\text{CH}_2)_4\text{CH}=\text{CHCH}_2\text{CH}=\text{CH}(\text{CH}_2)_7\text{CO}_2\text{CH}_3$	55.4
Methyl oleate CAS 112-62-9 $\text{C}_{17}\text{H}_{33}\text{CO}_2\text{CH}_3$	21.3
Methyl palmitate CAS 112-39-0 $\text{C}_{15}\text{H}_{31}\text{CO}_2\text{CH}_3$	11.8
Methyl linolenic CAS 301-00-8 $\text{CH}_3(\text{CH}_2\text{CH}=\text{CH})_3(\text{CH}_2)_7\text{CO}_2\text{CH}_3$	7.5
Methyl stearate CAS 112-61-8 $\text{C}_{17}\text{H}_{35}\text{CO}_2\text{CH}_3$	4.0

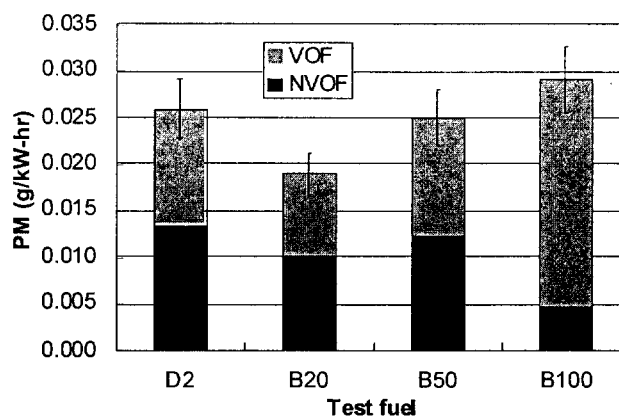
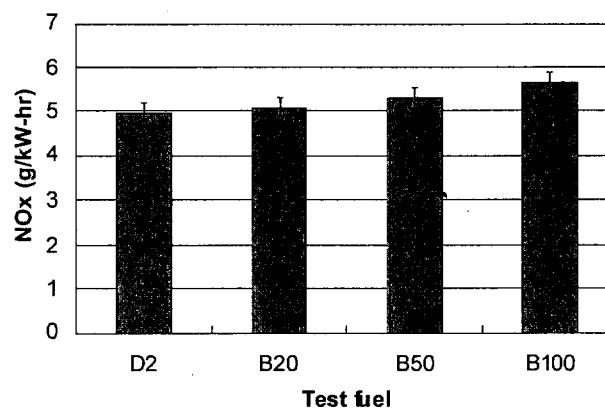
**Figure 1.** PM emissions.**Figure 2.** NO_x emissions.

Table 5. Summary of engine-out gaseous emissions.

Fuel	NO _x	HC	CO
	(g/kW-hr)		
D2	4.99	0.131	0.337
B20	5.11	0.115	0.302
B50	5.30	0.081	0.257
B100	5.65	0.040	0.202
	(percent of baseline diesel)		
B20	103%	88%	90%
B50	106%	62%	76%
B100	113%	31%	60%

Table 6. Summary of engine-out PM emissions.

Fuel	PM (NVOF)	PM (VOF)	Total PM
	(g/kW-hr)		
D2	0.0134	0.0125	0.0259
B20	0.0101	0.0089	0.0189
B50	0.0122	0.0128	0.0250
B100	0.0046	0.0245	0.0291
	(percent of baseline diesel)		
B20	75%	71%	73%
B50	91%	102%	96%
B100	34%	196%	112%

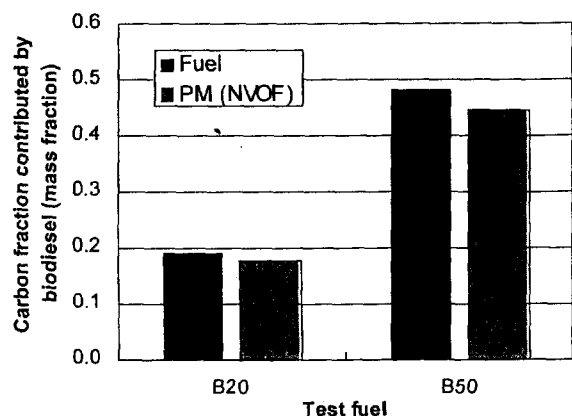


Figure 3. Fraction of carbon in fuel and in collected PM contributed by the biodiesel portion of the blended fuel.

Table 7. Fractional contribution of biodiesel to fuel carbon and PM carbon.

Test fuel	Mass fraction of fuel carbon from biodiesel	Mass fraction of PM carbon from biodiesel	Relative probability, <i>P</i>
B20	0.190	0.177	0.94
B50	0.483	0.447	0.92

Table 8. Fractional contribution of ethanol to fuel carbon and PM carbon (previously reported, from Reference 1).

Test fuel	Mass fraction of fuel carbon from ethanol	Mass fraction of PM carbon from ethanol	Relative probability, <i>P</i>
E10	0.054	0.027	0.50
E20	0.114	0.067	0.59